Synthesis and Characterization of Potassium Complexes Containing Terminal η^2-Pyrazolato Ligands

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The potassium complexes $[K(\eta^2\text{-}3,5\text{-}R_2pz)(\eta^6\text{-}18\text{-crown-}6)]$ (R = Ph, *t*Bu; pz = pyrazolato) were prepared by treatment of 3,5-diphenylpyrazole or 3,5-di-*tert*-butylpyrazole with potassium hydride in the presence of 18-crown-6. These complexes contain η^6-18-crown-6 and terminal η^2-pyrazolato ligands, and constitute the first examples of group 1 metal complexes with this pyrazolato ligand coordination mode. In contrast to $[K(\eta^2\text{-}3,5\text{-}Ph_2pz)(\eta^6\text{-}18\text{-crown-}6)]$ and $[K(\eta^2\text{-}3,5\text{-}tBu_2pz)(\eta^6\text{-}18\text{-crown-}6)]$, the aqua complex $[K(\eta^2\text{-}3,5\text{-}Me_2pz)(H_2O)(\eta^6\text{-}18\text{-crown-}6)]$ was obtained when 3,5-dimethylpyrazole was treated with potassium hydride and 18-crown-6 in the presence of a small amount of water. $[K(\eta^2\text{-}3,5\text{-}Me_2pz)(H_2O)(\eta^6\text{-}18\text{-crown-}6)]$ contains an η^2-pyrazolato ligand that is bent towards being co-facial with the best plane of the 18-crown-6 ligand, to allow hydrogen bonding between the pyrazolato ligand nitrogen atoms and the coordinated aqua ligand. The hydrogen bonding thus confers a novel terminal π-facial η^2-bonding mode to the pyrazolato ligand. All compounds were characterized by elemental analysis, NMR spectroscopy, and mass spectrometry.

Introduction

The coordination chemistry of metal complexes with pyrazolato (pz) ligands is currently a topic of considerable interest.[1−6] While many bridging coordination modes have been documented, pyrazolato ligands bonded to single metal centers (terminal coordination) are less common and are restricted to η^1,[1] η^2,[1e,2−4] and η^5.[5] The terminal η^1- and η^2-coordination modes reported to date involve donation of the in-plane nitrogen atom lone pairs to the metal centers, whereas only the rare η^5-bonding mode entails bonding with the out-of-plane π-orbitals of the aromatic pyrazolato ring.[5] Although many main group element pyrazolato complexes have been structurally characterized,[1,2,6] group 1 complexes are limited to a few examples with bridging pyrazolato ligands[7,8] and a small number containing tris(pyrazolyl)borate and related ligands.[9] Structurally characterized potassium pyrazolato complexes are restricted to $[(\mu\text{-}\eta^2{:}\eta^1{:}\eta^1\text{-}3,5\text{-}Ph_2pz)K(THF)]_6$,[8a] an erbium complex $[K\{Er(\eta^2\text{-}3,5\text{-}tBu_2pz)_4\}_n]$ with the potassium ion trapped in a bridged η^3-coordination mode,[8b] and a complex in which potassium is bonded to a structurally complex manganese-containing pyrazolato ligand through an η^5-interaction.[5b] No examples of terminal η^2-pyrazolato ligand coordination to a group 1 metal have been reported, most likely due to the propensity of these ligands to bridge between the large group 1 metal ions.

We have recently reported examples of the slipped η^2-coordination mode of triazolato and tetrazolato ligands to the $[K(18\text{-crown-}6)]^+$ fragment.[10] In these complexes, there was significant asymmetry in the potassium−nitrogen bond lengths ($\Delta_{K-N} = 0.35-0.60$ Å), and there were no obvious steric interactions that would cause such slipped pyrazolato ligand coordination modes. These results prompted us to investigate the coordination chemistry of analogous potassium pyrazolato complexes. Herein we report the synthesis, structure, and properties of several pyrazolato complexes of the $[K(\eta^6\text{-}18\text{-crown-}6)]^+$ fragment. The new complexes contain terminal η^2-pyrazolato ligands, and represent the first structurally characterized group 1 pyrazolato complexes with this coordination mode.

Results and Discussion

The synthetic chemistry is shown in Scheme 1. Treatment of equimolar quantities of potassium hydride, 3,5-diphenylpyrazole or 3,5-di-*tert*-butylpyrazole, and 18-crown-6 in tetrahydrofuran afforded colorless solids after filtration and removal of the solvent. However, the crude products could not be purified by recrystallization in common organic solvents or by other methods. Infrared spectra of the crude products show strong, broad stretches centered at approximately 3400 cm^{-1}, which suggest the presence of water in the products. Since commercial 18-crown-6 could form a hydrate, the solutions were further treated with excess potassium metal in refluxing tetrahydrofuran to eliminate any water that might be associated with the 18-crown-6. Follow-

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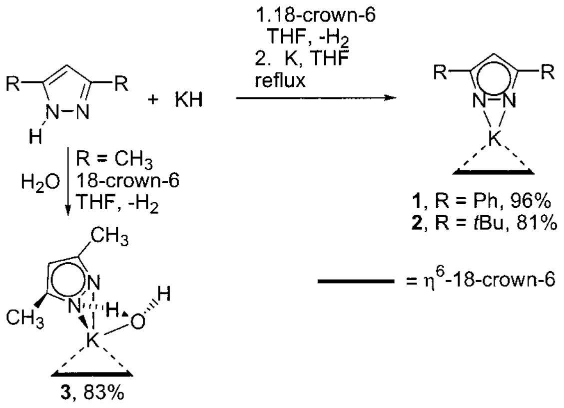
ing this treatment, the products were purified in several different ways. Filtration of the hot reaction solution and then allowing this solution to cool slowly to room temperature led to the direct crystallization of [K(η^2-3,5-Ph_2pz)(η^6-18-crown-6)] (**1**, 96%). The infrared spectrum of **1** does not show any absorption band near 3400 cm^{-1}, suggesting a water-free formulation. The complex [K(η^2-3,5-*t*Bu_2pz)(η^6-18-crown-6)] (**2**) did not crystallize from tetrahydrofuran on cooling after filtration. Removal of the tetrahydrofuran under reduced pressure afforded crude **2** as a colorless solid. Recrystallization from toluene at −20 °C afforded analytically pure **2** in a 81% yield as colorless crystals. There are no absorption bands at around 3400 cm^{-1} in the infrared spectrum of **2**. Due to the presence of the lipophilic *tert*-butyl groups, **2** is soluble in common organic solvents. By contrast, **1** is only soluble in polar solvents such as methanol and hot tetrahydrofuran. Attempts were made to prepare a 3,5-dimethylpyrazolato complex that was analogous to **1** and **2**. Treatment of equimolar quantities of potassium hydride, 3,5-dimethylpyrazole, and 18-crown-6 in tetrahydrofuran, followed by hot filtration of the reaction solution, led to colorless single crystals of [K(η^2-3,5-Me_2pz)(H_2O)(η^6-18-crown-6)] (**3**, 83%) on cooling of the tetrahydrofuran solution, without the need for further treatment with potassium metal. A crystal structure as described below reveals the presence of coordinated water. All attempts to prepare the water-free 3,5-dimethylpyrazolato analogue of **3** have thus far failed, and only **3** has been isolated. Apparently, **3** is highly crystalline and precipitates as soon as it forms. Further treatment of **3** with excess potassium metal as for **1** and **2** afforded a product that was only slightly soluble in tetrahydrofuran. This product gave complex ^{1}H NMR spectra and was not pursued further. Complexes **1**−**3** are thermally stable at room temperature and are unaffected by exposure to relatively dry ambient air for a few minutes. However, the complexes are hygroscopic and lose crystallinity upon extended exposure to ambient atmosphere. For this reason, **1**−**3** were handled under dry argon in this study.



Scheme 1

^{1}H and $^{13}C\{^1H\}$ NMR spectra, infrared spectra, and element analysis data are consistent with the formulations of **1**−**3**. In addition, the X-ray crystal structures of **1** and **3** were determined and are described below. The ^{1}H NMR spectra of **1**−**3** show resonance signals for the pyrazolato ligand, as well as resonances at about δ = 3.6 ppm for the protons of the 18-crown-6 ligand. A broad resonance at δ = 5.4 ppm in the ^{1}H NMR spectrum of **3** in [D_4]methanol is assigned to the protons of the aqua ligand. It is not clear if the water molecule is still coordinated to the potassium ion in **3**, or if it has been displaced by the methanol solvent. The infrared spectrum of **3** displays a broad absorption at 3400 cm^{-1}, which is assigned to the stretches associated with the aqua ligand. This band did not disappear completely even after **3** was heated at 100 °C for 15 h, suggesting strong bonding between the potassium ion and oxygen atom of the aqua ligand. The mass spectra of **1**−**3** show a parent ion at *m*/*z* = 303, which is consistent with the [K(18-crown-6)]$^+$ moiety.

Complexes **1** and **3** were structurally characterized by X-ray crystallography, the crystal data are given in Table 1. Perspective views of **1** and **3** are shown in Figure 1 and Figure 2, respectively, and an extended diagram that emphasizes the hydrogen bonding of **3** is given in Figure 3. We were unable to solve the X-ray crystal structure of **2** due to disorder in the crystals, but its solid-state structure is presumably very similar to that of **1**.

Complex **1** contains the η^2-3,5-diphenylpyrazolato and η^6-18-crown-6 ligands, and there are no significant intermolecular contacts (Figure 1). The potassium−nitrogen bond lengths [2.722(3), 2.766(4) Å] are similar and are consistent with idealized η^2-bonding. These bond lengths are within the range of those found in [(μ-η^2:η^1:η^1-3,5-Ph_2pz)K(THF)]$_6$ (K−N 2.716−2.869 Å).[8a] The potassium−oxygen bond lengths range between 2.78−2.95 Å, and are similar to other structurally characterized complexes containing [K(η^6-18-crown-6)]$^+$ fragments.[11] The angle formed between the plane of the pyrazolato C_3N_2 core and the best plane of the six oxygen atoms of the 18-crown-6 ligand is 85.01(10)°. Such an arrangement is consistent with donation of the in-plane lone pairs of the nitrogen atoms to the potassium ion, and is very similar to the η^2-coordination mode that has been documented in many main group element complexes.[1e,2] The potassium ion is located 0.710(2) Å above the best plane of the 18-crown-6 ligand oxygen atoms, towards the side with the pyrazolato ligand. This arrangement certainly facilitates bonding to the pyrazolato ligand. Selected bond lengths and angles for **1** are presented in Table 2.

Complex **3** contains the η^2-3,5-dimethylpyrazolato, η^6-18-crown-6 and aqua ligands. The aqua ligand hydrogen atoms are engaged in both intramolecular and intermolecular hydrogen bonding with the pyrazolato ligand. A view of the molecular structure is shown in Figure 2 and a view emphasizing the hydrogen bonding is contained in Figure 3. The potassium−nitrogen bond lengths are 2.955(3) and 3.138(3) Å. These bond lengths are longer than those in **1** due to the higher coordination number at the potassium ion (9 versus 8). In fact, the potassium−nitrogen bond lengths in **3** are even longer than would be expected when the coordination number increases by one, and support the idea that

Table 1. Summary of crystallographic data for **1** and **3**

	1	**3**
Formula	$C_{27}H_{35}KN_2O_6$	$C_{17}H_{33}KN_2O_7$
M	522.67	416.55
T (K)	295(2)	295(2)
Crystal system	monoclinic	monoclinic
Space	$P2_1/n$	$P2_1/n$
a (Å)	9.4714(10)	12.9297(15)
b (Å)	22.622(3)	8.7945(9)
c (Å)	13.9001(18)	19.436(2)
α (°)	90	90
β (°)	108.449(3)	92.730(2)
γ (°)	90	90
V (Å^{-3})	2825.2(6)	2207.6(4)
Z	4	4
$d_{\text{calcd.}}$ (g/cm^3)	1.229	1.253
Absorption coefficient (mm^{-1})	0.229	0.278
F(000)	1112	896
Crystal size (mm)	0.40 × 0.20 × 0.10	0.24 × 0.20 × 0.10
θ range (deg)	1.79 to 28.35	1.94 to 28.32
Limiting	$-12 \leq h \leq 11$; $0 \leq k \leq 30$; $0 \leq l \leq 18$	$-17 \leq h \leq 17$; $0 \leq k \leq 11$; $0 \leq l \leq 25$
No. of reflections collected	20327	16023
No. of independent reflections	6564 (Rint = 0.080)	5264 (Rint = 0.051)
No. of data/restraints/parameters	6564/0/326	5264/0/355
GOF/F^2	0.866	0.793
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0588$; $wR_2 = 0.1369$	$R_1 = 0.0475$; $wR_2 = 0.1226$
R indices (all data)	$R_1 = 0.2191$; $wR_2 = 0.1957$	$R_1 = 0.1727$; $wR_2 = 0.1859$
Largest diff. peak/hole (e·Å^{-3})	0.213/−0.392	0.205/−0.283

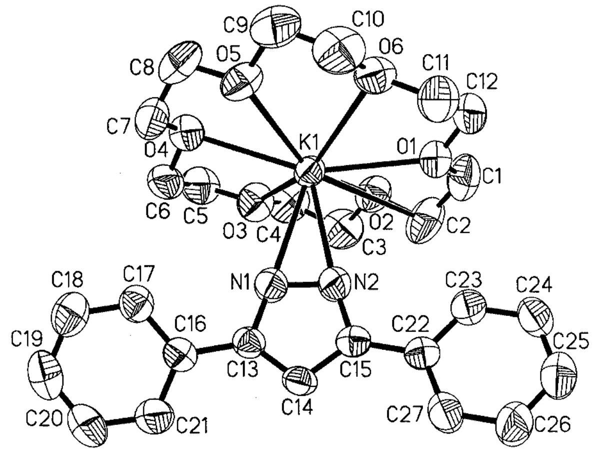


Figure 1. Perspective view of **1** with thermal ellipsoids at the 50% probability level

Table 2. Selected bond lengths (Å) and angles (°) for **1**

K−N(1)	2.766(4)
K−N(2)	2.722(3)
K−O(1)	2.775(3)
K−O(2)	2.860(3)
K−O(3)	2.816(3)
K−O(4)	2.954(3)
K−O(5)	2.864(3)
K−O(6)	2.917(3)
N(1)−N(2)	1.362(4)
N(1)−C(13)	1.351(5)
N(2)−C(15)	1.358(5)
C(13)−N(1)−K(1)	177.3(3)
C(15)−N(2)−K(1)	174.2(3)
N(1)−K−N(2)	28.72(9)

3 contains a new pyrazolato coordination mode. The longer potassium−nitrogen bond lengths in **3** may also arise as a result of the less basic pyrazolato ligand π-orbitals donating to the potassium ion (i.e. less optimum ionic bonding). The potassium−oxygen bond lengths are 2.848(3) Å for the aqua ligand and 2.84−3.07 Å for the 18-crown-6 ligand. These values are similar to or slightly longer than the related values found in **1** and other [K(η^6-18-crown-6)]$^+$ fragments.[11] The angle formed between the plane of the pyrazolato C_3N_2 core and the best plane of the 18-crown-6 ligand oxygen atoms is 24.40(14)°, which indicates that the planes of the 18-crown-6 ligand oxygen atoms and the pyrazolato ligand are almost coplanar. This situation is very different from that of **1**, where the pyrazolato ligand core plane is nearly perpendicular to the best plane of the 18-crown-6 ligand oxygen atoms. The distance of the nitrogen atoms from the best plane of the 18-crown-6 ligand oxygen atoms is 3.409(3) Å for N(1) and 3.711(3) Å for N(2), indicating that the pyrazolato ligand core plane is twisted slightly relative to that of the 18-crown-6 ligand. The potassium ion is located 0.976(1) Å above the best plane of the 18-crown-6

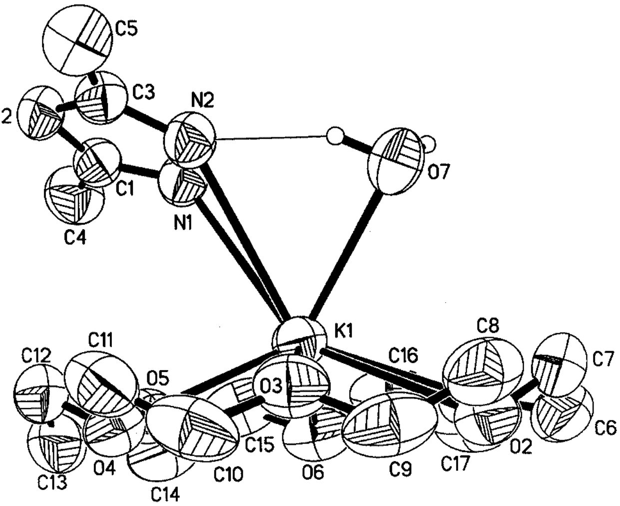


Figure 2. Perspective view of **3** with thermal ellipsoids at the 50% probability level

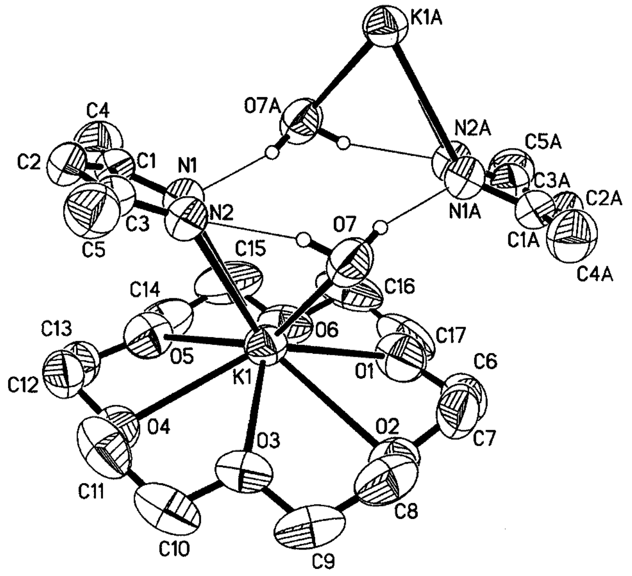


Figure 3. Perspective view of **3** that emphasizes the intramolecular and intermolecular hydrogen-bonding interactions; thermal ellipsoids are at the 50% probability level

Table 3. Selected bond lengths (Å) and angles (°) for **3**

K−N(1)	2.954(3)
K−N(2)	3.138(3)
K−O(1)	2.837(3)
K−O(2)	3.071(3)
K−O(3)	2.912(3)
K−O(4)	2.980(3)
K−O(5)	2.836(3)
K−O(6)	3.045(3)
K−O(7)	2.847(3)
N(1)−N(2)	1.381(4)
C(1)−N(1)−K	140.1(2)
C(3)−N(2)−K	142.8(2)
N(1)−K−N(2)	25.98(7)

ligand oxygen atoms. This value is larger than that of **1**, and reflects the larger coordination number in **3** and the differing coordination modes in the two complexes. Selected bond lengths and angles for **3** are given in Table 3.

Inspection of the hydrogen bonding in **3** reveals that one hydrogen atom of the aqua ligand is intramolecularly hydrogen bonded to N(2) of the pyrazolato ligand, with a nitrogen−hydrogen distance of 2.00(5) Å, a N(2)−O(7) distance of 2.813(7) Å, and a N···H−O angle of 154(3)°. The other hydrogen atom of the aqua ligand is intermolecularly hydrogen bonded to N(1) of an adjacent molecule, with a nitrogen−hydrogen distance of 2.01(5) Å, a N(1′)−O(7) distance of 2.883(7) Å, and N···H−O angle of 164(3)°. The intermolecular hydrogen bonding thus leads to dimeric species within the crystal that are connected by 10-membered $H_4N_4O_2$ rings.

The bending of the pyrazolato ligand in **3** towards the plane of the 18-crown-6 ligand and its slight twisting relative to this plane could have several origins. Accommodation of the aqua ligand in **3** requires that the pyrazolato ligand moves on the face of the coordination sphere to facilitate formation of the new potassium−oxygen bond. Such motion would necessarily lead to a reduction of the angle between the planes of the 18-crown-6 and pyrazolato ligands. However, there is a further bending of the pyrazolato ligand toward the 18-crown-6 ligand, as is seen by the 140.7(3)° angle between the KN_2 and C_3N_2 planes. With the observed distortions, the in-plane (and more basic) nitrogen atom lone pairs point more directly toward the aqua ligand hydrogen atoms, which presumably optimizes intramolecular and intermolecular hydrogen bonding. The stronger intramolecular hydrogen bonding to N(2) could infer some less basic character on this atom, which is a possible origin for the longer K−N(2) bond length and the slight twisting of the C_3N_2 plane relative to that of the 18-crown-6 ligand oxygen atoms. The disposition of the pyrazolato ligand in **3** requires that there is at least some donation of electron density to the potassium ion from the out-of-plane π-orbitals on the nitrogen atoms of the pyrazolato ligand. Idealized π-η^2-pyrazolato ligand coordination to a single metal center would have an angle of about 90° between the MN_2 and C_3N_2 planes. Such a coordination mode has not been reported, although this coordination mode has been documented in an ytterbium complex containing a phosphorus−antimony analog of a pyrazolato ligand.[4c] This ytterbium complex has no hydrogen bonding. However, the pyrazolato ligand in **3** represents a distortion that is significantly towards an idealized π-η^2-pyrazolato ligand, and this bonding arrangement is clearly driven by the hydrogen-bond formation with the aqua ligand. The predominately ionic bonding expected for a group 1 salt probably allows for low energy distortions of the ligands about the coordination sphere. The potassium−nitrogen bonding mode in **3** resembles that observed in lanthanide complexes containing μ-η^2:η^2 pyrazolato ligands,[12] since the latter coordination mode also demands donation of some electron density from the out-of-plane π-orbitals on the nitrogen atoms of the pyrazolato ligand.

This work documents the first examples of monomeric terminal η^2-pyrazolato ligand coordination to a group 1 metal. The 18-crown-6 ligand saturates the coordination sphere in **1** in such a way that the 3,5-diphenylpyrazolato ligand can just be accommodated by **1**. Optimal ionic bonding then leads to the observed η^2-pyrazolato ligand. In our recent report,[10] the triazolato and tetrazolato complexes [K(iPr$_2$C$_2$N$_3$)(18-crown-6)] and [K(PhCN$_4$)(18-crown-6)] have asymmetric potassium−nitrogen distances (Δ_{K-N} = 0.35−0.60 Å) and there was no evidence for steric interactions that would promote such asymmetric bonding of the heterocyclic ligands. By contrast, **1** contains an essentially idealized η^2-pyrazolato ligand (Δ_{K-N} = 0.044 Å). The nitrogen atom lone pairs in the pyrazolato ligands are definitely more basic than those of the 1,2,4-triazolato and tetrazolato ligands,[13] and the better donor characteristics of the pyrazolato ligands may then facilitate the η^2-coordination mode relative to the more nitrogen-rich heterocyclic ligands. The first examples of terminal η^2-1,2,4-triazolato and tetrazolato ligand coordination have been reported in the past several years.[2d,10,14]

Use of the less sterically demanding 3,5-dimethylpyrazolato ligand leads to the aqua complex **3**, which contains a novel η^2-pyrazolato ligand coordination mode. There is an analogy between **3** and the metal complexes containing slipped cyclopentadienyl ligands.[15−17] In two crystallographically characterized complexes containing terminal η^2-cyclopentadienyl ligands, [Mg(η^5-Cp)(η^2-Cp)(NH$_2$[CH(CH(CH$_3$)$_2$]$_2$)][16a] and [Mg(η^5-Cp)(η^2-Cp)(NH$_2$C(CH$_3$)$_3$](THF)],[16b] the η^2-cyclopentadienyl ligands are stabilized through intramolecular and intermolecular N−H···C hydrogen bonding.[16a] This is similar to the stabilization of the pyrazolato ligand in **3**. The complexes Mg(tBu$_2$pz)$_2$(tBupzH)$_2$ [14] and Nd(Me$_2$pz)$_3$(Me$_2$pzH)$_2$(py)[18] contain intramolecular N−H···N hydrogen bonding that appears to enforce η^1-bonding of the pyrazolato ligands.

Experimental Section

General: All reactions were performed under dry argon using standard Schlenk and dry box techniques. Solvents were distilled from various drying agents under argon prior to use. 3,5-Diphenylpyrazole, 3,5-dimethylpyrazole, and 18-crown-6 were purchased from commercial sources. 3,5-Di-*tert*-butylpyrazole was prepared according to literature methods.[19]

^{1}H and ^{13}C{^{1}H} NMR spectra were obtained in dry, degassed [D$_4$]methanol and [D$_8$]tetrahydrofuran, and were referenced to the residual proton or carbon atom resonances of these solvents. Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake−Buchler HBI digital melting point apparatus and are uncorrected.

[K(η^2-3,5-Ph$_2$pz)(η^6-18-crown-6)] (1): A mixture of 3,5-diphenylpyrazole (2.20 g, 10.0 mmol), potassium hydride (0.42 g, 10.5 mmol), and 18-crown-6 (2.77 g, 10.5 mmol) in tetrahydrofuran (100 mL) was stirred at room temperature for 15 h, after which time hydrogen evolution was complete. This solution was further treated with excess potassium (0.50 g, 13 mmol), and the suspension was refluxed for 0.5 h. The hot solution was filtered through a 2-cm pad of Celite and **1** formed as colorless single crystals as the solution cooled (5.02 g, 96%). M.p.: 173 °C. ^{1}H NMR (CD$_3$OD, 23 °C): δ = 7.35, 7.81 (mult, 10 H, Ph-*H*), 6.94 (s, 1 H, C*H*), 3.53 (s, 24 H, O−C*H$_2$*). ^{13}C NMR (CD$_3$OD, 23 °C): δ = 150.73 (s, *C*−Ph), 133.87, 129.77, 128.59, 126.58, (4s, *C*, Phenyl ring), 100.44 (s, *C*H), 71.25 (s, O−*C*H$_2$). MS (EI): *m/z*: 303 ([K(18-crown-6)]$^+$, 100%). C$_{27}$H$_{35}$KN$_2$O$_6$ (522.7): calcd. C 62.04, H 6.75, N 5.36; found C 62.18, H 6.82, N, 5.40.

[K(η^2-3,5-*t*Bu$_2$pz)(η^6-18-crown-6)] (2): In a fashion similar to the preparation of **1**, treatment of 3,5-di-*tert*-butylpyrazole (1.80 g, 10.0 mmol) with potassium hydride (0.42 g, 10.5 mmol), 18-crown-6 (2.77 g, 10.5 mmol), and potassium (0.5 g, 13 mmol) in tetrahydrofuran afforded crude **2** as a tetrahydrofuran solution. After removal of the tetrahydrofuran under reduced pressure, the crude material was dissolved in toluene and cooled to −20 °C to afford **2** as colorless crystals (3.92 g, 81%). M.p.: 158 °C. ^{1}H NMR (C$_4$D$_8$O, 23 °C): δ = 5.53 (s, 1 H, C−*H*), 3.62 (s, 24 H, C*H$_2$*), 1.25 (s, 18 H, C*H$_3$*). ^{13}C NMR (C$_4$D$_8$O, 23 °C): δ = 157.78 (s, *C*−*t*Bu), 92.38 (s, *C*H), 71.02 (s, O−*C*H$_2$), 32.66 (s, *C*−CH$_3$), 25.71 (s, *C*H$_3$). MS (EI): *m/z*: 303 ([K(18-crown-6)]$^+$, 100%). C$_{23}$H$_{43}$KN$_2$O$_6$ (482.7): calcd. C 57.23, H 8.98, N 5.80; found C 57.35, H 8.86, N 5.72.

[K(η^2-3,5-Me$_2$pz)(H$_2$O)(η^6-18-crown-6)] (3): Treatment of 3,5-dimethylpyrazole (0.96 g, 10 mmol) with potassium hydride (0.42 g, 10.5 mmol) and 18-crown-6 (2.77 g, 10.5 mmol) in tetrahydrofuran (100 mL) at room temperature for 2 h, followed by reduction in volume to 50 mL under reduced pressure, and after standing for 48 h, afforded **3** as colorless crystals (3.45 g, 83%). M.p.: 145 °C. ^{1}H NMR (CD$_3$OD, 23 °C): δ = 5.80 (s, 1 H, C*H*), 5.4 (br, 2 H, *H$_2$*O), 3.61 (s, 24 H, O−C*H$_2$*), 2.19 (s, 6 H, C*H$_3$*). ^{13}C NMR (CD$_3$OD, 23 °C): δ = 145.50 (s, *C*−CH$_3$), 104.69 (s, *C*H), 71.35 (s, *C*H$_2$), 11.95 (s, *C*H$_3$). MS (EI): *m/z*: 303 ([K(18-crown-6)]$^+$, 100%). IR (Nujol, cm^{-1}): ν_{OH} = 3400 (s). C$_{17}$H$_{33}$KN$_2$O$_7$ (416.6): calcd. C 49.02, H 7.99, N 6.73; found C 48.99, H 7.89, N, 6.64.

X-ray Crystallography: Crystals of **1** (M = 522.67) and **3** (M = 416.55) were grown as described above and crystallized in the monoclinic crystal system with space group $P2_1/n$. Relevant details and data are summarized in Table 1. The crystals were mounted in thin glass capillaries under an argon atmosphere. Diffraction data were collected on a Bruker P4 four-circle diffractometer coupled to a Bruker CCD area detector at 295(2) K, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved from the Patterson maps using SHELX-97[20] and refined against F^2 on all data by full-matrix least-squares with the same program. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the model at their geometrically calculated positions and held riding or observed on a difference Fourier and refined. CCDC-201685 (**1**) and CCDC-201686 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk]. Structure searches were performed using the Cambridge Crystallographic Database, Version 5.24, November 2002.

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